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A STUDY OF THE CONCENTRATION AND ESTIMATION OF ORGANIC CHEMICAL COMPOUNDS IN RAW AND FILTERED SURFACE WATERS

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A STUDY OF THE CONCENTRATION AND ESTIMATION OF ORGANIC CHEMICAL COMPOUNDS IN RAW AND FILTERED SURFACE WATERS*

A knowledge of the kinds and concentrations of organic chemical compounds in surface waters is important and useful in studies concerned with tastes and odors in drinking water, natural purification of streams, analysis and tracing of industrial wastes, and toxic and other physiological effects on man and animal.

Direct analysis for most organic compounds is not usually possible due to the minute concentrations which normally occur in surface waters. This study describes a method for the concentration and estimation of organic compounds in raw and filtered surface water. Possible applications of the techniques presented are discussed.

Method of Concentration of Organic Compounds from Raw and Filtered Surface Waters

The concentration of the organic compounds in the waters tested is accomplished by passing from 5,000 to 75,000 gallons of water through small portable activated carbon filters. The average rate of flow of the water through the filter is approximately 0.1 to 0.6 gallons per minute. Figure 1 shows the simplest type of activated carbon filter for use on filtered or finished water. This unit consists of a 3-foot length of iron pipe 4 inches in diameter. Between 1,200 and 1,500 grams

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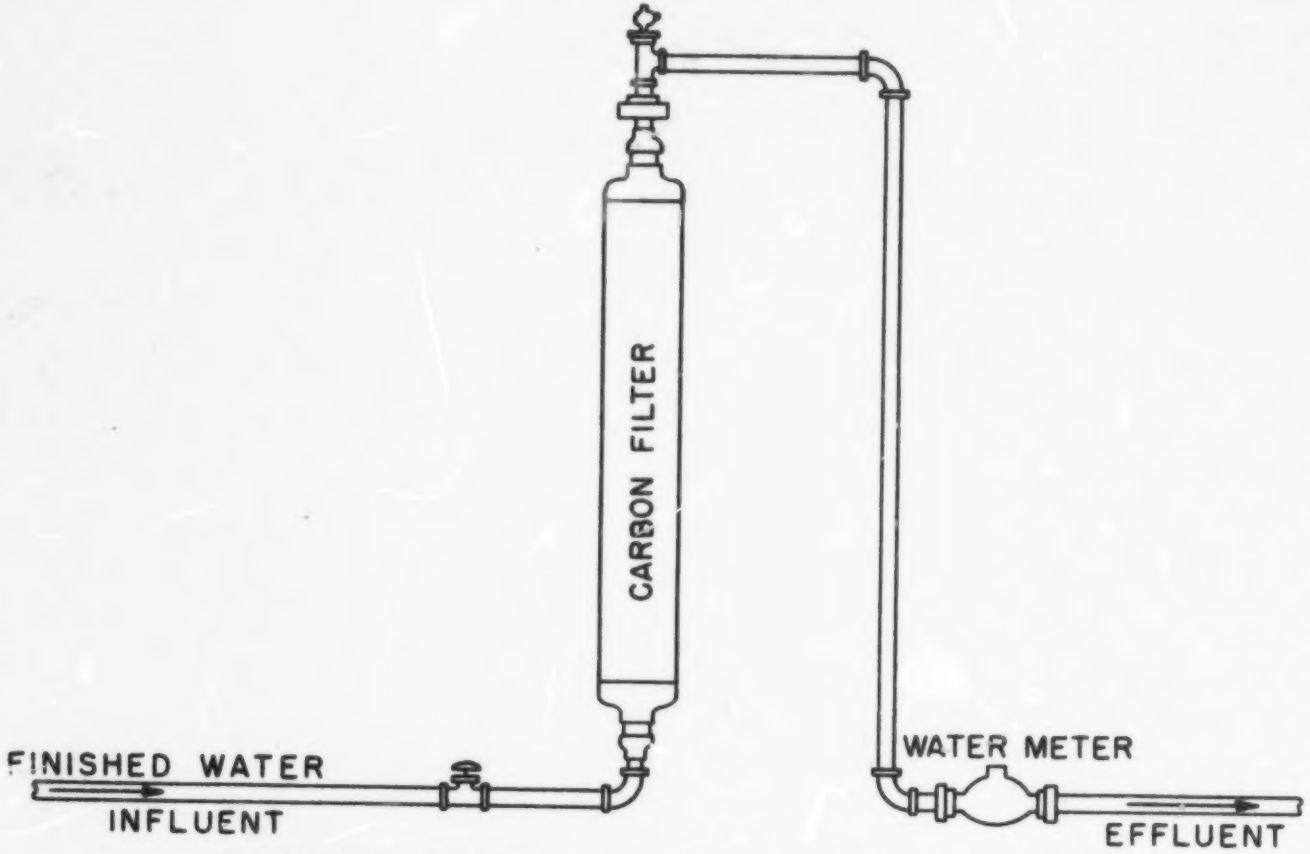
* Presented at the 117th National Meeting of the American Chemical Society, Detroit, Michigan, April 17-19, 1950.

FIGURE 1



CARBON FILTER INSTALLATION AS USED FOR SAMPLING FILTERED WATER FOR TRACE QUANTITIES OF ORGANIC CHEMICALS

of granular activated carbon are charged into this cylinder. The carbon is held in place by perforated cadmium-plated disks, equivalent to about a 16-mesh screen, soldered into the reducers at each end.

Figure 2 shows the assembly used when turbid or raw waters are sampled. The carbon filter is the same as that shown in Figure 1. It is preceded by an iron cylinder approximately half full of filter sand and fine gravel. Valves are arranged so that the sand filter may be by-passed, back-washed with the raw water or rinsed by filtering-to-waste. A minimum head of 10 feet of water is necessary for the effective operation of this unit.

A plastic filter is used for laboratory studies. It consists of a 4-foot length of plastic tubing, 3 inches in diameter. Carbon is held in place by a 60-mesh bronze screen at each end.

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Selection of Carbons

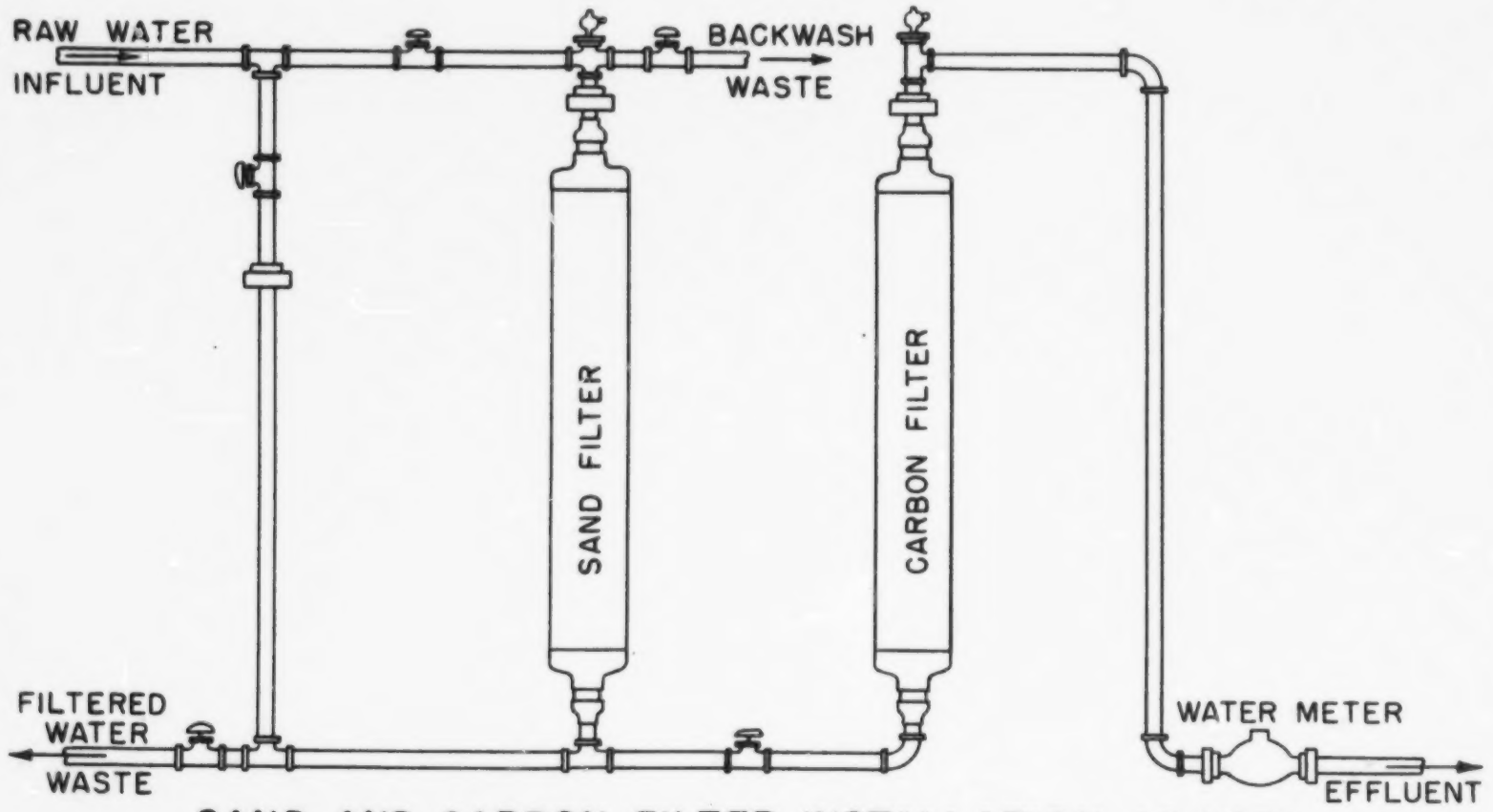
Two types of activated carbon were used in these studies. The field filters were charged with granular (4-10 mesh) Cliffchar and the laboratory filter was charged with unground Nuchar C-190 furnished by the Industrial Chemical Sales Division of West Virginia Pulp and Paper Company.

These carbons contain some ether extractable materials as received from the manufacturer. Results of ether extraction tests made with carefully purified ether are shown in Table I.

TABLE I

Carbon	Per Cent of Ether Extractable Materials
Cliffchar, granular	0.0117
Nuchar C-190, unground	0.0027

FIGURE 2



SAND AND CARBON FILTER INSTALLATION AS USED FOR SAMPLING TURBID WATER FOR TRACE QUANTITIES OF ORGANIC CHEMICALS

It will be noted that Nuchar C-190 carbon had less than one-fourth as much ether extractable material as does the Cliffchar carbon.

A comparison of the adsorptive ability of these carbons was made using Cincinnati tap water. Approximately 8,000 gallons of water were passed through each of two filters containing the respective carbons during the same period. The results of this test are shown in Table II.

It will be noted that approximately five times as much material was recovered from the same quantity of water using the C-190 carbon. However, the finer particle size of this carbon makes filtration of raw water difficult and the granular carbon was used in most of the preliminary field studies.

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Studies on Field Filters

Filters of the type described were placed in water plants at various cities on the Ohio River and at other locations having surface water supplies. An effort was made to include certain locations known to be subject to industrial waste pollution and others known to be free of such pollution. Results of these studies will be discussed later in this paper.

Analytical Procedures

After a quantity of water has been passed through the filters, they are returned to the laboratory and dismantled. The carbon is removed and air dried on a 60-mesh bronze screen. The carbon is then placed in a modified Soxhlet extractor of the type shown in Figure 3, and extracted

TABLE II

A Comparison of the Quantity of Organic Material Extracted from Equal Volumes of the Same Cincinnati Tap Water by Two Types of Activated Carbon

Type Carbon	Weight of Carbon Used	Total Organic Material Extracted*	
	grams	grams	P.P.B.**
Nuchar C-190	902	4.016	133
Cliffchar	1900	0.81	27

* The net weight after correction for organic extractable material from the carbon.

** Parts per billion

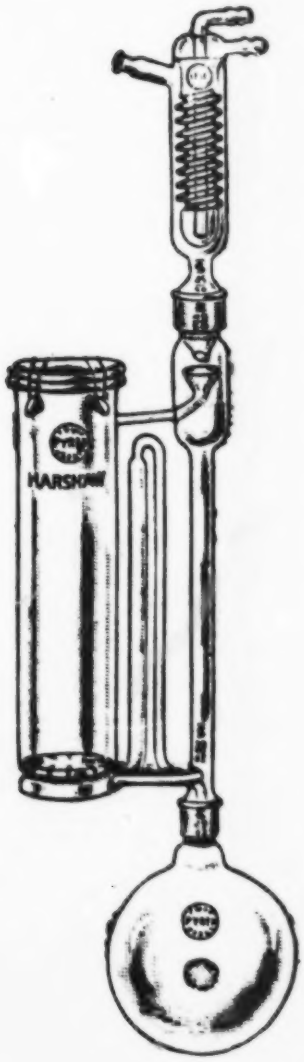

Figure 3

Large-Capacity Extraction Apparatus

with diethyl ether*. Great care must be exercised in starting the extraction because a large amount of heat of adsorption is evolved. We have found it reasonably safe to slowly add carbon to the cold ether previously placed in the Soxhlet extractor.

After extraction the ether extract is evaporated to a volume of 25 ml. anhydrous sodium sulphate is added to the ether solution and the whole is allowed to stand 48 hours. The ether solution is then filtered and the residue is washed with four 5 ml. portions of anhydrous ether. The residue is discarded. The ether solutions are combined in a tared flask and gently evaporated in the hood. The flask and contents are dried in a vacuum desiccator over calcium chloride and weighed. The net weight represents the total ether extractable material found on the carbon.

The ether extractable material is now subjected to group separation which is effected according to a modification of the method of Shriner and Fuson [3], as shown in Figure 4.

The dry ether soluble residue is taken up in 25 ml. of ether and placed in a separatory funnel. It is extracted using four 10 ml. portions of 5 per cent hydrochloric acid in which is dissolved 20 per cent sodium chloride. The hydrochloric acid-sodium chloride extracts are combined and rendered alkaline with 5 per cent sodium hydroxide solution. The resulting mixture is extracted with four 10 ml. portions of ether. The

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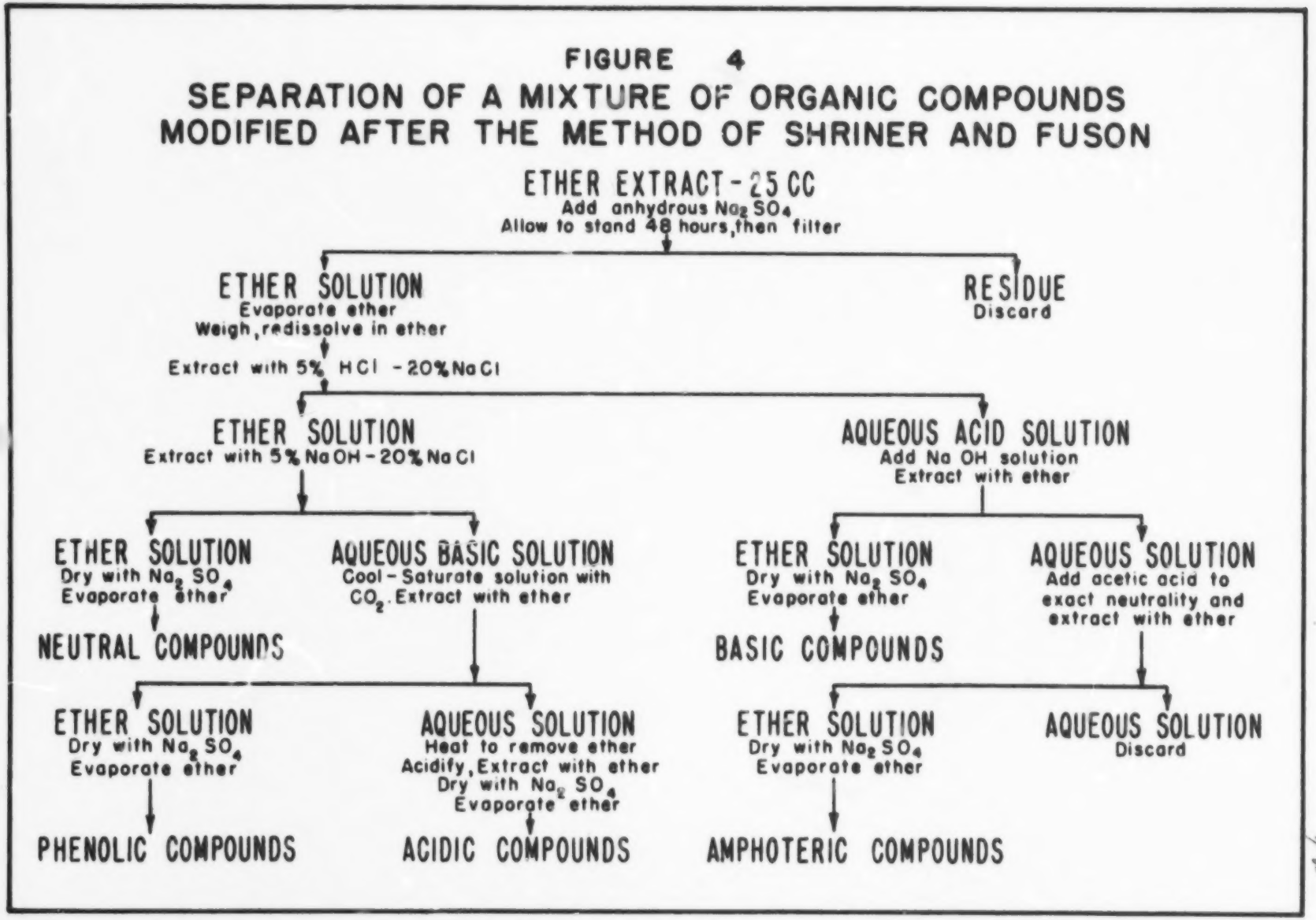
* A good grade of ether is selected. Care must be used to keep at a minimum the formation of peroxides in the ether. The U.S.P. test for peroxides in ether should be applied. Purification of ethers may be accomplished as follows: The ether is shaken with acidulated ferrous sulfate, washed with distilled water and dried with anhydrous calcium chloride. After standing several days over the calcium chloride, the ether is filtered through Whatman No. 12 filter paper and distilled.

FIGURE 4

SEPARATION OF A MIXTURE OF ORGANIC COMPOUNDS MODIFIED AFTER THE METHOD OF SHRINER AND FUSON



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ether layers are combined and dried over anhydrous sodium sulphate. The dried ether solution is filtered to remove the sodium sulphate. The ether is evaporated and the residue is weighed after desiccation over calcium chloride. The residue is composed of organic basic compounds, largely amines.

The basic water solution now contains the amphoteric compounds. It is carefully neutralized with acetic acid and extracted with five 10 ml. portions of ether. The ether extracts are combined and dried as previously. The ether is evaporated and the residue is desiccated over calcium chloride and weighed. This residue is composed of amphoteric compounds.

The ether layer remaining from the hydrochloric acid extraction is now extracted with four 10 ml. portions of 5 per cent sodium hydroxide containing 20 per cent sodium chloride. A soapy emulsion formed at this point may be broken by the addition of a drop of ethyl alcohol or a little more water. The ether layer is dried with anhydrous sodium sulphate, filtered and evaporated. The residue remaining is weighed as a mixture of neutral organic compounds.

The neutral residue so obtained is usually a complex mixture. No general method of analysis is available. Certain methods of separation, however, may be useful. The methods commonly resorted to are fractional crystallization, distillation and sublimation. Remarkable separation may be achieved by these methods in many instances. When separation is completed the individual components may be further classified.

The sodium hydroxide-sodium chloride solutions are combined, cooled, and saturated with gaseous carbon dioxide. The carbon dioxide saturated

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solution is now extracted five times with 5 ml. portions of ether, dried, and evaporated. The residue is weighed after drying and is composed largely of phenolic compounds.

The sodium bicarbonate-sodium chloride solution is now gently heated and stirred to remove any dissolved ether. It is then cooled, made acid to litmus with dilute hydrochloric acid and extracted with four 10 ml. portions of ether. After drying and evaporation of the ether, the residue is weighed. This residue is composed of strong acids and highly acidic phenols.

Throughout the whole procedure semi-micro or micro equipment is used wherever possible. Sodium chloride is added to all aqueous extractants to decrease the solubility of the ether and generally to render more quantitative separations. All volumes are kept as low as possible. Because of the small amounts of materials involved thorough washing and shaking in extractions is necessary.

When separation of the groups is completed a micro qualitative test for the elements nitrogen, sulphur and chlorine is made. The determination for nitrogen and sulphur is made according to the method of Feigl (1).

Results

Carbon (Cliffchar) filters were placed in service at six water plants along the Ohio River from Midland, Pennsylvania to Louisville, Kentucky during the spring of 1949. An additional carbon filter was placed in service at Columbus, Ohio (Scioto River). After a metered volume of water had passed through the carbon filters the filters were returned to the laboratory and the carbon subjected to the treatment

described above.

Pertinent data relative to the sampling locations, period of sampling, quantity of water passed through the filters, and the total quantity of organic matter extracted from the carbons are presented in Table III. The total amount of organic material extracted, as shown in the last column of Table III, varied from 9.3 to 32 parts per billion (p.p.b.). These values may be subject to significant error due to variable filtration rates and metering errors. It is interesting to note that the extract from the Columbus, Ohio sample contained appreciable quantities of organic compounds. This supply is relatively free from industrial pollution.

Cincinnati tap water was passed through a filter containing Nuchar C-190 carbon. The ether extract from the carbon was deep yellow in color. On evaporation a black viscous residue of foul odor was obtained. Elemental analysis of this residue indicated the presence of nitrogen, sulfur and halogen. The residue was then subjected to qualitative group separation according to the scheme shown in Figure 4.

The HCl-NaCl extraction was continued until most of the yellow color was extracted. The NaOH-NaCl-H_2O extraction yielded three layers. The top ether layer was colored amber while the lower aqueous layer changed to an orange color indicative of phenolic materials. Between these two layers a dark oily middle layer of a tarry consistency was noted. The three layers were separated and the tarry mixture was recovered.

The middle layer was found to be soluble in very dilute sodium hydroxide but insoluble in 5 per cent or stronger sodium hydroxide as well as in water, hydrochloric acid solution and petroleum ether. In addition, this compound was soluble in ethyl alcohol, benzene, carbon disulphide and

TABLE III

Total Anhydrous Organic Extract in Various Surface Water Supplies

Location of Water Plant	Filter In Service		Sampling Point	Quantity of Water*	Organic Material Extracted	
	From	To		Gals	grams	P.P.B.**
Midland, Pa.	2/14	7/14	Filter Effluent	19,275	1.275	17.5
Wheeling, W. Va.	2/2	8/9	Filter Effluent	20,560	1.575	21.0
Huntington, W. Va.	5/28	7/25	Finished Water	23,550	1.795	21.0
Pomeroy, O.	1/24	5/11	Filter Effluent	40,000	1.420	9.3
Cincinnati, O.	6/1	8/1	Raw Water	4,000	0.485	32.0
Louisville, Ky.	4/14	8/3	Filter Effluent	28,000	1.160	10.7
Columbus, O.	5/28	9/15	Filter Effluent	80,800	4.000	13.0

* Metered flow of water through Cliffchar carbon

** Parts per billion

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ether. Crystallization could not be induced from any of these solvents or mixtures thereof. The compound was purified by dissolving in very dilute sodium hydroxide and reprecipitating with dilute hydrochloric acid. After several such reprecipitations a light brown amorphous powder was obtained.

It was thought that this substance might be a complex phenol and that the anomalous behavior was caused by the sodium salt. Subsequent tests, however, did not indicate the compound to be of phenolic nature. The compound could not be acetylated, and on reaction with Gibbs reagent gave a negative response. Using the Liebermann-Storch reaction a positive violet color was obtained indicating a rosin type compound. A terpene-like odor was noted.

A positive test for chlorine was obtained in the phenolic group. Reaction with the Gibbs reagent gave a green color indicative of chlorinated phenols. Separation of the individual phenols was not attempted. The phenolic groups as separated had the typical phenol odor.

The acid groups were characterized by an odor similar to caproic acid. The group was isolated as a viscous almost solid mass of brown color. Micro distillation yielded a residue of very high boiling point. It had the general properties attributed to high molecular fatty acids. It is conjectured that the origin of these acids may be the large amount of laundry wastes dumped into the river. The odor of the basic group is best described as a tobacco like odor. Pyridine or pyridine type compounds were shown to be present using the micro test of Feigl [2].

The organic neutral compounds appear to be the largest group of compounds isolated. This group is characterized by a particularly offensive odor. No identifications of the constituents of this group have as yet been attempted. However, the pine splinter-hydrochloric acid test was positive on the other extract. The red color formed is indicative of pyrrole or pyrrole derivatives. Their presence in the neutral groups would in many cases be consistent with solubility considerations.

In the analysis of a different filter which was in operation along the Ohio River below a refinery relatively large amounts of hydrocarbons were isolated from the neutral group. It was subjected to micro steam distillation and the distillate was extracted with ether. Upon evaporation of the ether and solution of the residue in fuming sulphuric acid a floating layer resulted which is highly indicative of aliphatic hydrocarbons.

The amphoteric group is characterized by little or no odor. This is consistent with the presence of more than one polar group. No separation or identification of this group has been attempted.

Possible Applications of Technique

1. Taste and Odor Studies

Tastes and odors in water supplies may arise from industrial and domestic wastes or from natural causes such as the growth and decay of aquatic plants and animals. In any case, most of the compounds causing the objectionable tastes and odors are organic in nature.

The use of the concentration, extraction and separation procedures presented in this paper provides a method for obtaining

sufficient quantities of the organic compounds for study. By actual taste and odor tests the organic groups or individual compounds most likely to cause tastes and odors may be determined. In addition to taste and odor considerations, these organic compounds may be studied as to their effect on water treatment processes, their rate of natural purification in streams, and their treatment for removal from water or wastes. Threshold concentrations of taste and odor were determined on the total organic extract of certain samples and on the various organic groups separated. The results of these tests are shown in Table IV.

Examination of the table reveals that 3 to 25 p.p.b. of the total organic extracts from the various waters gave detectable odors when tested in the laboratory by the water dilution method. No attempt has been made in this study to compare the threshold odor concentrations of the various organic extracts with the actual odors occurring in the water supplies from which the extracts were obtained. Carbon filters were purposely set up to receive the rapid sand filter effluents at the water plants to avoid the possible effects of chlorination on the taste and odor producing substances.

The extract from the Columbus, Ohio water supply produced detectable odor in a concentration of 3 parts per billion. As previously pointed out the Columbus water supply is not subject to industrial pollution. The extract obtained from Cincinnati tap water produced detectable odor at a concentration of 25 parts per billion. This water had undergone complete treatment including breakpoint chlorination.

TABLE IV

Lowest Concentration of Organic Extract Detectable by Water Dilution Method of Odor Testing

Source of Water*	Lowest Concentration Detected by Odor Test parts per billion
Huntington, W. Va.	13
Wheeling, W. Va.	25
Louisville, Ky.	13
Columbus, O.	3
Pomeroy, O.	6
Cincinnati, O.	25
A. Organic Groups:	
1. Phenolic	50
2. Neutral	11
3. Organic Acids	160

* All sources of water were filter effluents before chlorination, except at Cincinnati where water treatment includes breakpoint chlorination.

The phenolic, neutral and organic acid groups which were separated from the Cincinnati tap water extract were tested for odor producing characteristics. The neutral group was detected at a concentration of 11 p.p.b., and the phenolic and acid groups at a concentration of 50 and 160 p.p.b. respectively.

2. Tracing Industrial Wastes

Isolation of the organic compounds gives a clue as to the type of industry responsible for contributing the waste material. By this means a contributor of a given waste may be identified. The method has also proved useful in the direct examination of certain industrial wastes.

3. Study of Reactions in Dilute Solution

The concentration method is useful in the study of certain reactions in dilute solution. The reactions of chlorine and phenol in dilute solution are being studied in our laboratory. To obtain a sufficient amount of the reaction product for study, large quantities of the dilute solutions are treated with active carbon. The carbon is removed by filtration followed by ether extraction and recovery of the product formed in the reaction. The isolation of these chlorinated-phenolic products has been accomplished and their identification is presently being investigated. Other reactions that may be studied include the products formed by use of chlorine dioxide and ozone when added to various compounds present in water.

4. Possible Basis for Physiological Study

The physiological effect, if any, of small concentrations of organic compounds in drinking water has not been studied. The method presented is helpful in providing sufficient material for studies of a physiological nature.

SUMMARY

A procedure for concentrating minute amounts of organic compounds in raw and filtered surface waters, based on passing the water through an activated carbon filter and then extracting the dried carbon with diethyl ether, has been applied to waters from seven municipal water plants. The ether-extracted organic material varied from 9.3 to 32 parts per billion. These results may be subject to significant error due to variable filtration rates and metering errors.

The organic compounds obtained can be partially resolved into various organic groups by utilization of an organic analytical scheme based on differential solubility. Qualitative examination of this material can be made. Study of this material may provide useful information on the role of organic chemicals in taste and odors in drinking waters, industrial wastes, stream purification and possible physiological effects.

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